Indian J. Phys. **47**, 513-527 (1973)

Ligand field theory of the magnetic and optical properties of cobalt (II) ammonium and potassium sulphate hexahydrates

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(*Received* 14 *September* 1972)

This work was undertaken with a view to study the magnetic and optical properties of cobalt (II) ammonium and potassium tutton salts in the light of the ligand field theory, refined by us for the common octahedrally coordinated $[Co(6H_2O)]^{2+}$ complex ion in these salts. For this purpose, refined experimental measurements on magnetic anisotropies, susceptibilities between 300°K–68°K and the optical absorption studies at room and liquid nitrogen temperatures, of single crystals of the salts, were undertaken. The results have been correlated with the theoretical expressions and the values of the ligand field parameters calculated. These parameters gave informations on the nature and effect of the ligand field acting in these complexes, and the fine structure of the infrared and optical electric spectra in these salts.

INTRODUCTION

The magnetic properties of the cobalt Tutton salts of the general formula— $Co(XSO_4)_2, 6H_2O$, where X is a monovalent alkali metal ion, are of deep interest since the pioneering workers Jackson (1928), Krishnan *et al* (1933, 1936), Bose (1948) and others showed that for these salts the magnetic anisotropies are remarkably large and the susceptibilities deviate considerably from Curie Law at low temperatures. An approximate theory of the paramagnetic susceptibility of $Co(NH_4SO_4)_2, 6H_2O$ was first given by the classical work of Schlapp & Penney (1932) based on the assumption of a rhombic crystalline-electric field. But this did not take into consideration the number of Co^{2+} ions in the unit cell and the secular determinant could be solved only for two extreme cases of very low and very high electric fields. The paramagnetic resonance study of Bleaney *et al* (1951) proved the presence of a uniaxial symmetry in the g-values for the ammonium-salt, and only a slight orthorhombicity in the potassium one. This was closely followed by the work of Abragam & Pryce (1951) who obtained expressions for the g-values for both tetragonal and trigonal crystalline electric fields for the $3d^7.{}^4F$. Co^{2+} ionic complexes and attempted to explain their optical absorption spectra. The secular determinant, required for the eigen value

solution in each case, was exactly diagonalized by an ingenious simplification of the expression for the lowest orbital level $^4T_{1g}$ under the crystal-field, and the spin-orbit coupling and the axial-field perturbations were simultaneously applied on the modified ground orbital states. Uryu (1956) tried to fit the experimental low temperature susceptibility data with the theoretical expressions based on the same eigen-functions as mentioned above. However, Bose *et al* (1961) pointed out an error in the computational work of Uryu (1956), and themselves obtained the correct expressions for g-values and magnetic susceptibilities. The purpose of the present work is to apply in this case the more general Ligand Field Theory, which incorporates the idea of anisotropic covalency effects (Bose *et al* 1960–1965)

Guha Thakurta *et al* (1966) measured the magnetic anisotropies and susceptibilities of the potassium and ammonium cobalt sulphate hexahydrates between 300°–68°K, very accurately, using a much more sophisticated experimental set up than used by the previous workers in this laboratory (Dutta 1956, Mazumdar 1965), necessitated by the high refinement of the theoretical expressions and the results have been examined in this paper in the light of this theory. Furthermore, the optical absorption spectra for both these salts have been observed by us at liquid nitrogen temperatures, in order to investigate the nature and cause of the colour-changes observed by Mazumdar (1965) in these salts

Crystallographic Data

Detailed crystallographic data for $Co(NH_4SO_4)_2\,6H_2O$ have been published by Montgomery *et al* (1968), and the relevant details from their measurements, *e.g.* space-group, cell-dimensions etc , are given in table 1. As these Tutton-salts belong to monoclinic system, the principal crystalline susceptibility χ_3-axis coincides with the crystallographic b-axis, χ_2 makes an angle θ with a-axis and χ_1 makes an angle ψ with c-axis, related by the equation $\beta = \pi/2+\theta+\psi$, where β is the monoclinic obtuse angle (*see* table 1 for values of θ and β). As shown by Bleaney *et al* (1951) the ionic magnetic ellipsoid in $Co(NH_4SO_4)_2.6H_2O$ has an axial symmetry, the ionic g-values are $g_z = g_{\|}$ and $g_x = g_y = g_\perp$ also $g_{\|} > g_\perp$. Then the ionic susceptibilities may be taken as $K_z = K_{\|}$, $K_x = K_y = K_\perp$ where (x, y, z) axes are usually along the three body diagonals of the water octahedron with the Co^{2+} ion at the centre. The angle ϕ made by $K_{\|}$ with χ_1 can be directly measured from the epr study and also calculated from the measured crystalline magnetic anisotropies, since in the present uniaxial case we have, for $K_{\|} > K_\perp$ (as required by epr finding $g_{\|} < g_\perp$) :

$$\left.\begin{aligned} \cos 2\phi &= \frac{(\chi_1-\chi_3)}{2(\chi_1-\chi_2)-(\chi_1-\chi_3)} \\ K_{\|}-K_\perp &= 2(\chi_1-\chi_3)-(\chi_1-\chi_3) \end{aligned}\right\} \quad \ldots (1)$$

TABLE 1. $Co(NH_4SO_4)_2.6H_2O$

$a = 9{\cdot}209$ Å, $b = 12{\cdot}475$ Å, $c = 6{\cdot}227$ A, $\beta = 106{\cdot}57$,
$\chi_{ac} = \theta = 60°6'$ (our measurement)

Bond Lengths (Å)	χ_1	χ_2	χ_3
$Co—O_7 = 2{\cdot}107$	163	45	50
$Co—O_5 = 2{\cdot}105$	46	164	48
$Co—O_6 = 2{\cdot}08$	48	38	65

ϕ from e.p.r. study (Bleaney 1951) = 34° at 20°K
ϕ from our study = 35° at 300°K

The values of ϕ obtained from both the studies are very close as shown in table 1. Inspection of the X-ray data in table 1 shows that the octahedron is axially distorted along $Co–O_9$ bond (figure 1) which appears therefore to be the $K_{||}$ axis.

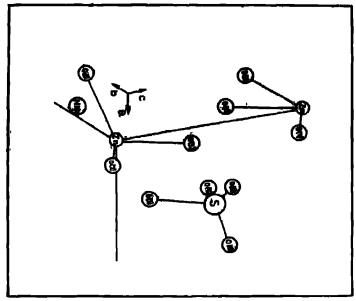

Fig. 1 X-ray structure of the isomorphous $Zn(NH_4SO_4)_2\ 6H_{20}$ (Montgomery *et al* 1964).

In that case, by equation 1, according to magnetic and epr data, $Co–O_9$ direction ($K_{||}$-axis) should make an angle $\phi = 38°$ with the χ_1 direction. To verify this, we next calculated the orientation of all the three Co–O bond directions, with respect to the principal crystalline susceptibility axes system (table 1), using the x-ray data and our magnetic data involving the measurement of θ value. Inspection of table 1 shows that there is no unique correspondence between the apparent X-ray symmetry axis of the ion and the symmetry axis of the magnetic ellipsoid, from magnetic studies, which is not strange considering quantum mechanical distinctions in the interpretations of the two sets of axes.

In the case of $Co(KSO_4)_2.6H_2O$, where epr data gives $g_z = 6{\cdot}56$, $g_x = 2{\cdot}30$, $g_y = 3{\cdot}3$, suggesting a small but appreciable orthorhombic distortion, the calculation of the ionic susceptibilities is more difficult in the absence of detailed X-ray crystallographic data on this salt. We can, however, still interpret meaningfully

the magnetic properties on the assumption of an axial ligand field, provided we always keep in mind the obvious limitations of such an approximation.

Ligand Field Theory

For the free Co^{2+} ion, the $[A]\,3d^7$ configuration under a weak Russel-Saunders coupling gives rise to a ground ^4F orbital level followed by a ^4P at $\sim$1400 cm^{-1} above it. In the complex $[Co(6H_2O)]^{2+}$ the degeneracies of these two term levels are partially removed by the action of the weak perturbations such as the crystalline electric field and the spin-orbit coupling interaction, giving rise to the fine structure of the electronic spectrum as discussed by earlier workers (Abragam & Pryce 1951, Bose *et al* 1961). The two-fold Kramers spin degeneracy is however retained except under an exchange or magnetic field Now considering the more realistic picture of the charge cloud overlap between the Co^{2+} ion and ligand water oxygen atoms, we express the cubic field levels in terms of the corresponding $3d$-subshell configurations :

$$^4T_{1g}(F) \equiv [t_{2g}{}^1 e_g{}^2], \qquad ^4A_{2g} \equiv [t_{2g}{}^3],$$

$$^4T_{2g}(F) \equiv [t_{2g}{}^2 e_g{}^1], \qquad ^4T_{1g}(P) \equiv [e_g{}^1 t_{2g}{}^2].$$

The three degenerate orbitals levels of $^4T_{1g}(F)$ is expressed as the following molecular orbitals formed by single hole product functions in the three hole formalism :

$$\phi_1 = |e^a_{x^2-y^2} e^b_{z^2} t^c_{xy}|,$$

$$\phi_2 = |e^a_{x^2-y^2} e^b_{z^2} t^c_{yz}|,$$

$$\phi_3 = |e^a_{x^2-y^2} e^b_{z^2} t^c_{zx}|.$$

where due to overlap of ligand-metal orbitals in O_h symmetry we know (Tinkham 1956)

$$t_{xy} = \alpha_1 d_{xy} - \beta_1(\pi_{1x}+\pi_{2y}+\pi_{4x}+\pi_{5x}) \qquad \text{(similarly for } t_{yz} \text{ and } t_{zx})$$

$$e_{x^2-y^2} = \alpha_2 d_{x^2-y^2} - \beta_2(\sigma_1+\sigma_4-\sigma_2-\sigma_5) \qquad (\quad ,, \quad ,, \quad e_{z^2-r^2})$$

Next we express the lowest orbital triplet state $^4T_1(F)$ as :

$$|+> = \frac{1}{\sqrt{2}} |(\phi_3 + i\phi_2)>$$

$$|0> = \frac{1}{\sqrt{2}} |\phi_1>$$

$$|-> = \frac{1}{\sqrt{2}} |(\phi_3 - i\phi_2)>.$$

When calculating the energies of these molecular states $|0>$, $|+>$ and $|->$, under the different remaining perturbations, *i e.* the axial field and the s–o coupling which are expressed in terms of the sub-Himiltonian **H** where:

$$\mathcal{H}' = \Delta(1-l_z')-\alpha\lambda l_z'S_z-\alpha'\lambda(l_x'S_x+l_y'S_y).$$

(Abragam & Pryce 1951), we have to evaluate the matrix elements of l' and $\lambda l'$ S operators on the various single hole d-orbitals constituting these molecular orbital states Following Griffiths (1957) detailed calculations show that if we confine our attention to the lowest triplet $^4T_{1g}$ states only, then the effect of the molecular orbital procedure is to reduce the spin-orbit coupling constant anisotropically (Bose *et al* 1965) to $\alpha\lambda_{||}$ and $\alpha'\lambda_{\perp}$ and the orbital angular moment in the ground manifold to the components αKl_z, $\alpha' K_{\perp} l'_x$ $(= \alpha' K_{\perp} l'_y)$ where the 's are the orbital reduction factors Thus the sub-Hiamiltonian

$$\mathcal{H}' = \Delta(1-l_z')-P_{||}l_z'S_z-P_{\perp}(l_x'S_x+l_y'S_y), \text{ and } P_{\perp} = \alpha'\lambda_{\perp},\ P_{||} = \alpha\lambda_{||}$$

Next proceeding with the magnetic field perturbation on the ground states we arrive at the following expressions for ionic susceptibilities Kp $(p = \| \text{ or } \perp)$ in the parallel and perpendicular directions as :—

$$K_z \quad \frac{N\beta^2}{kZ}\sum_{r=1}^{6}\left[\frac{1}{T}\,G_{1q}{}^r \exp\left(-\frac{E_r-E_1}{kT}\right)+2k\,G_{2q}{}^r \exp\left(-\frac{E_r-E_1}{kT}\right)\right.$$

where the symbols have the usual meanings, and Z is the partition function Using the convention for the suffix $q = z$ and $q = x = y$, corresponding to $p = \|$ and $p = \perp$ respectively, we get :

z-direction :

$$G^1{}_{1z} = \tfrac{1}{2}[2\{(a_i{}^2-c_i{}^2)Q_{||}+3a_i{}^2+b_i{}^2-c_i{}^2\}+\{(3a_i{}^2-c_i{}^2)\nu_1+b_i\nu_2+(\sqrt{6}a_ib_i-\sqrt{8}b_ic_i)\nu_3\}]^2$$

$$G^2{}_{1z} = 2\{3a_j{}^3+b_j{}^2(1-Q_{||})\}^2$$

$$G^4{}_{1z} = 2(3-Q_{||})^2$$

$$G^1{}_{2z} = \sum_{i\neq n}\frac{2}{(E_n-E_1)}\{(a_ia_n-c_ic_n)Q_{||}+(3a_ia_n+b_ib_n-c_ic_n)\}^2$$

$$G^2{}_{2z} = \sum_{j\neq m}\frac{2}{(E_m-E_1)}\{3a_ma_j+(1-Q_{||})b_jb_m\}^2$$

$$G^4{}_{2z} = 0.$$

x-direction :

$$G^1{}_{1x} = \tfrac{1}{2}\{4(-Q_{\perp}b_ic_i+\sqrt{3}a_ic_i+b_i)^2+(b_i{}^2\nu_4+c_i{}^2\nu_5+\sqrt{3}a_ic_i\nu_6+\sqrt{2}b_ic_i\nu_7)\}^2$$

$$G^2{}_{1x} = G^4{}_{1x} = 0$$

$$G^1{}_{2x} = \sum_{i\neq n} \frac{t_{in}}{E_n - E^i} + \sum_{j\neq l} \frac{v_{lj}}{E_j - E_l}$$

$$G^j{}_{2x} = \sum_{i\neq j} \frac{v_{ij}}{E_j - E_i} + \sum_{j\neq 4} \frac{w_j}{E_4 - E_j}$$

$$G^4{}_{2x} = \sum_{j\neq 4} \frac{w_j}{E_j - E_4}$$

using the convention, $i = 1, 2, 6$ and $j = 3, 5$. The ν's are as defined by Abragam *et al* (1951). In the above expressions

$$t_{in} = 2\{-Q_\perp(b_i c_n + b_n c_i) + \sqrt{3} a_i c_n + 2 b_i b_n + \sqrt{3} a_n c_i\}^2$$

$$u_{ij} = 2\{-Q_\perp(a_i a_j + b_i b_j) + (\sqrt{3} a_j b_j + 2 b_j c_j)\}^2$$

$$w_j = 2\{-Q_\perp a_j + \sqrt{3} b_j\}^2$$

$$Q_\parallel = \alpha\kappa_\parallel, \quad Q_\perp = \alpha'\kappa_\perp/\sqrt{2}; \quad (\kappa\text{'s are orbital reduction factors})$$

$$a_i = \frac{(\sqrt{3}/2)P_\parallel b_i}{(3/2)P_\parallel - E_i'}, \qquad c_i = \frac{\sqrt{2}P_\perp b_i}{P_\parallel/2 - E_i}, \quad a_i^2 + b_i^2 + c_i^2 = 1$$

$$a_j = \frac{(\sqrt{3}/2)P_\perp b_j}{\Delta - E_j}, \qquad a_j^2 + b_j^2 = 1.$$

and the energies are as follows :

$$E_1 = P_\parallel x_1, \quad E_2 = P_\parallel x_2, \quad E_6 = P_\parallel x_3,$$

where x_1, x_2, x_3 are the roots of the 3×3 matrix obtained from the secular determinants (Bose *et al* 1960) and $P_\parallel \alpha = \alpha\lambda_\perp$, $P_\perp = \alpha'\lambda_\perp$,

$$E_3 = \tfrac{1}{2}[\Delta - P_\parallel/2 - \sqrt{(\Delta + P_\parallel/2)^2 + 6P_\perp^2}]$$

$$E_5 = \tfrac{1}{2}[\Delta - P_\parallel/2 + \sqrt{(\Delta + P_\parallel/2)^2 + 6P_\perp^2}]$$

$$E_4 = -3/2P_\parallel,$$

Optical Absorption Studies

Optical absorption study of paramagnetic crystals is capable of giving direct informations on the ligand field orbital levels under suitable conditions. With a view to study the ligand field characteristics of $Co(NH_4SO_4)_2.6H_2O$ and $Co(KSO_4)_2.6H_2O$ crystals and also to investigate the nature and cause of the visual colour changes in these crystals at low temperatures, as reported by Mazumdar *et al* (1965), polarized spectra were obtained between the optical range of 18–25 KK, at room and nitrogen temperatures (figure 2a,b) with a double beam spectrophotometer set up in our laboratory by Mukherjee *et al* (1969).

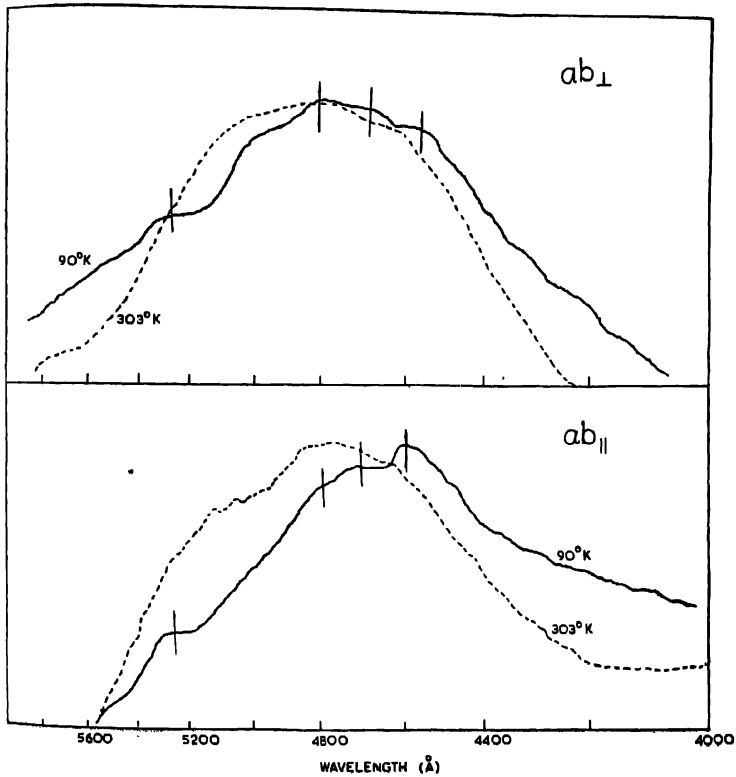

Fig. 2a. Absorption spectra for $Co(NH_4\ SO_4)_2\ 6H_2O$ at room and nitrogen temperatures.

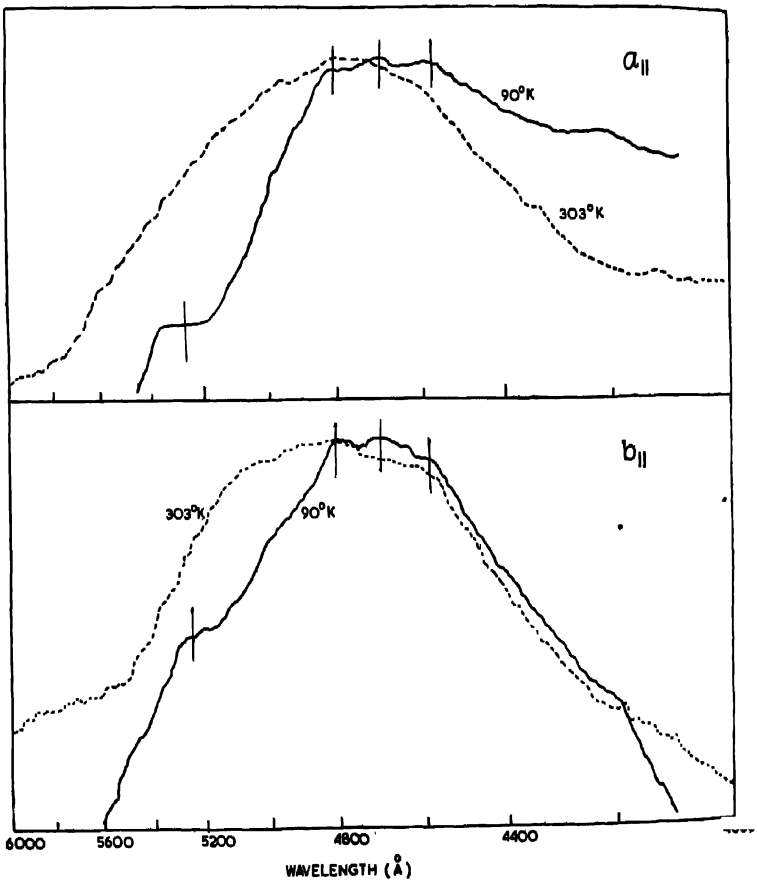

Fig. 2b Absorption spectra for $Co(K\ SO_4)_2\ 6H_2O$ at room and nitrogen temperatures.

A broad band around ~ 20 KK was observed at room temperature in both the crystals, which was partially resolved at the lowest temperature, showing several humps (figure 2a,b). A similar band was observed in $CoSO_4.7H_2O$ by Holmes *et al* (1964) and in $CoSiF_6$, $6H_2O$ by Mazumdar *et al* (1964), arising from the superimposition of the bands : $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$. In table 2 we have given the positions of this band and its components for the two Co^{2+} Tutton salts, the hexahydrated fluosilicate and the heptahydrated sulphate. Comparing the results for these four salts, we observe certain common characteristics For example, (*i*) the broad band occurs at around 19 KK to 20 KK at room temperatures, suggesting that the cubic field component is more or less equal in all these salts, having $Dq \approx 950$ cm^{-1} (Balhausen 1962), (*ii*) the band shape and the position of the components differ, however, from salt to salt; (*iii*) also in all these cobalt complexes, the low temperature spectra exhibit small blue shifts, being 0·6 KK in the Tutton salts (table 2) and 1·1 KK and 0 9 KK, respectively, for the hexahydrated fluosilicate and heptahydrated sulphate The blue shift may be attributed to contraction of the lattice as also to the freezing off of some of the vibronic transitions in the longer wave length region at low temperatures

TABLE 2

Polarization direction	Crystal	Band position (KK) at	
		Room temp	90°K
ab plane	$Co(NH_4SO_4)_2,6H_2O$	20.7	19.0, 21.0
ab plane		2 80	— —
a axis ‖	$Co(KSO_4)_2,6H_2O$	20 0	19 0, 21 2
b axis ‖		—	— —
	$CoSO_4$, $7H_2O$	19 8	19 0, 20.7
	$CoSiF_6$, $6H_2O$	19.5	19.0, 20.6

This may generally explain the colour changes observed in the Tutton salts and in the fluosilicate. However, it may be mentioned here that a different interpretation to this phenomenon in the particular case of the fluosilicate was given by Mazumdar *et al* (1965) to explain the peculiar phase transition below ~253°K, observed in this salt; (*iv*) the most interesting feature in all these compounds is the appearance of a component at ~19 KK at liquid nitrogen temperature which was interpreted differently in the case of the hexahydrated fluosilicate and heptahydrated sulphate by the earlier workers. For example, in the latter case, Holmes *et al* (1964) studied the thermal effect on the components of this

band and identified the component at 19 KK appearing at low temperatures to be due to the transition between a component of $^4T_1(P)$ and the ground $^4T_1(F)$ level, in which case the position of this component ought to have varied from crystal to crystal, since the splitting of the $^4T_2(P)$ due to the lower symmetric field varies from salt to salt, even in an isomorphous series (*see* later) In the case of the fluosilicate on the other hand, Mazumdar *et al* (1965) associated the appearance of the band, at 19 KK at low temperatures with the 'phase change' found by them to occur in the crystal at 253°K, accompanied by a change in the crystal symmetry. However, no such phase change has yet been observed in the other three crystals, in which also the same band appeared at low temperatures; (*v*) lastly, our results show that in all these spectra this component is weaker than the other components.

Koide (1959) has calculated the oscillator strength for the following transitions .

$$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) = 1{\cdot}7 \times 10^{-4}$$

$$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) = 4{\cdot}8 \times 10^{-6}$$

Thus only if we take this component at 19 KK to be due to $^4T_{1g}(G) \rightarrow {}^4A_{2g}(F)$ transition, we can account for its weaker transition characteristics as well as the appearance of this band in all these four spectra of the common ionic complex $[Co(6H_2O)]^{2+}$, and also the fact that the position of this band (having no components) remains the same in all these compounds Moreover, the Dq value can be calculated, since we have for $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition $18\,Dq \approx 19$ KK, *i.e* $Dq = 1050$ cm^{-1}, which is close to the value of 950 cm^{-1} quoted above (Ballhausen 1952). The appreciable shift in the band at ~21 KK from salt to salt becomes obvious as this is then due to the transition $^4T_{1g}(G) \rightarrow {}^3T_{2g}(P)$, which consists of two components and the CG of which changes from salt to salt, since the anisotropic field is known to be more structure sensitive (Bose *et al* 1951) A more detailed investigation of the same salts at hydrogen temperatures will be useful for confirming the assignments of the components of the splittings due to the lower symmetric field, which are useful for magnetic studies.

Results and Discussions of the Magnetic Anisotropy and Susceptibility Measurements

The method of measurements of magnetic anisotropies and the experimental results of the cobalt(II) ammonium and potassium double sulphate hexahydrates have been given in details elsewhere (Guha Thakurta 1966). It may be mentioned here that the 'null' method for the measurements of crystalline anisotropies has been applied there giving results (table 3) of much higher accuracy than the 'Critical Torque' method used by earlier workers.

Low temperature mean susceptibility $\bar{K}$ ($= \frac{1}{3}(K_{\parallel}+2K_{\perp})$), was measured with a very sensitive electro-dynamic Curie-balance and a cryostat working in the range of 400°–65°K (Ghosh *et al* 1970), and the results are given in tables 3a and 3b.

TABLE 3a $CoSO_4$, $(NH_4)_2SO_4$, $6H_2O$

Temp (°K)	$(\chi_1-\chi_2)$ $\times 10^6$	$(\chi_1-\chi_3)$ $\times 10^6$	$(K_{\parallel}-K_{\perp})$ $\times 10^6$	(ΔKT) $\times 10^4$	$\bar{K}$ $\times 10^6$	p_f^2
303	3011 8	1715 4	4308.2	1305 2	9730	23.58
280	3565 7	2108 4	5023.0	1406 4	10490	23.49
260	4156.8	2510.3	5803.3	1508.8	11260	23.41
240	4878.5	3001.7	6755.3	1621.2	12140	23 30
220	5760 3	3617.7	7902.9	1738 6	13180	23.18
200	6872.5	4400.0	3945.0	1869.0	14410	23.04
180	8283 9	5401.2	11166	2009 8	15880	22.84
160	10105	6742 2	13468	2154 8	17680	22.62
140	12515	8576.5	16453	2903 4	19960	22 34
120	15652	10930	20374	2444.8	22870	21 94
100	19550	14502	24598	2459.8	26700	21.35
80	24500	18300	30700	2456 0	31720	20 29
68	27898	21622	34174	2323 8	35320	19.20

TABLE 3b. $CoSO_4$, K_2SO_4, $6H_2O$

Temp. (°K)	$(\chi_1-\chi_2)$ $\times 10^6$	$(\chi_1-\chi_3)$ $\times 10^6$	$(K_{\parallel}-K_{\perp})$ $\times 10^6$	(ΔKT) $\times 10^4$	$\bar{K}$ $\times 10^4$	p_f^2
303	2490 5	1835.2	3145.8	953.17	9936	24.07
280	2913.9	2152.0	3677.8	1029.7	10740	24.06
260	3357.9	2502.3	4213.5	1095 5	11560	24.04
240	3890.6	2940.2	4861 2	1166 6	12510	24.00
220	4532.2	3530.0	5552.1	1221.4	13610	23 95
200	5317.5	4306.4	6328 6	1265.7	14920	23 87
180	6311.7	5185.1	7438.3	1338.9	16500	23.75
160	7562.9	6190 2	8934.8	1429.5	18410	23.56
140	9198 9	7538 8	11059	1548 2	20740	23.22
120	11451	9248.9	13653	1638.3	23670	22.72
100	14320	11501	17139	1713.9	27510	22.00
80	18328	14403	22203	1780.2	33200	21.24
60	21907	16552	27262	1853.8	38250	20.80

In order to interpret these experimental findings in terms of the ligand-field theory, we use the method of parametral fitting of these experimental results

in the expressions for susceptibilities at different temperatures deduced in an earlier section. The theoretical expressions for magnetic susceptibilities involve the following parameters *i e.* $P_{\|}$, $P_{\perp}$, $Q_{\|}$, $Q_{\perp}$ and Δ, all of which we assume to be temperature independent to start with By extensive trial and error we have obtained a set of values for these parameters consistent with the optical absorption data as shown in tables 4a and 4b, such that the experimental results for anisotropies ΔK and the mean susceptibilities K are exactly fitted with the corresponding theoretical expressions at 100°K and the deviations between the experimental and the theoretical results at other temperatures in the range 300°K to 20·3°K is minimum It may be noted that while calculating the principal g-values and susceptibilities K we have neglected the admixtures coming from the ν's (Abragam and Pryce 1951) which are usually small.

TABLE 4a. $CO(NH_4SO_4)_2$, $6H_2O$

Parameter Δ, P, Q	g	Temp °K	$K_{\|}-K_{\perp}$	$\overline{K}\times 10^6$
$\Delta = 700$ cm^{-1}	$g_{\|}$ = (5 59)	300	4,114 (4,308)	10,390 (9.827)
$P_{\|} = 194$ 4	= (6 45)*	200	9,295 (9,345)	15,230 (14,410)
$P_{\perp} = 230$		100	24,620 (24,600)	26,730 (26,700)
$Q_{\|} = 1.200$	$g_{\perp}$ = (3 2) (3 06)*	68	36,020 (34,170)	35,500 (35,320)
$Q_{\perp} = 1$ 096		(20.3)†	115,830(130,900)†	95,940 (93,600)+

TABLE 4b $Co(KSO_4)_2$ $6H_2O$

Parameters Δ, P, Q	g	Temp. °K	$K_{\|}-\overline{K}_{\perp}\times 10^6$	$\overline{K}\times 10^6$
Δ = 300 cm^{-1}	$g_{\|}$ = (6.62)	300	3,745 (3,169)	10,160 (10,030)
$P_{\|} = 224$ 1	(6 55)*	200	7,890 (6,328)	15,670 (14,920)
$P_{\perp}$ = 230 4		100	17.270 (17,160)	27,670 (27,510)
$Q_{\|}$ = 0 800	$g_{\perp}$ = (3 07) (2, 50)*	68	24,260 (27,260)	33,560 (38,250)
$Q_{\perp}$ = 1.174				

The values in the parenthesis are the experimental results obtained by us,
* Bleaney *et al* (1951). † Uryu (1956)

Considering first the case of $Co(NH_4SO_4)_2$ $6H_2O$, inspection of table 4a shows that, for the best fit of the experimental results with the theory, the axial field splitting Δ of the lowest $^4T_{1g}$ orbital level is 700 cm^{-1} (earlier workers Abragam & Pryce 1951 and Bose *et al* (1961) reported $\Delta \sim 1000$ cm^{-1}) and the other parameters P's and Q's are as given in the table 4a. Using these parameters in the

expressions for susceptibilities, we find that the lowest group of the three Kramers doublets are spread over about 1400 cm^{-1} only, consequently the angular momentum operator along with the spin-orbit interaction (both reduced anisotropically by the anisotropic ligand field) strongly couples these lowest levels, arising from the $^4T_{1g}$ group level, between themselves and also with the different upper ones, *e g*, $^4T_{2g}(F)$, $^4A_{2g}(F)$ and ^4P levels, thereby contributing appreciably to the mean susceptibilities rasing its value much above the spin-only value and also producing large ionic anisotropies

Deviations from Curie law occurs even at quite high temperature regions (figure 3), which is expected bacause the second order Zeeman terms in the expressions for susceptibilities are comparable to the first order term.

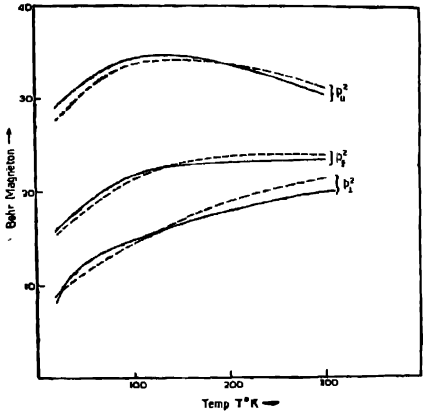

Fig. 3 The mean and anisotropic moment square VS temperature curves for $Co(NH_4SO_4)_2\ 6H_2O$(—exptl, .. Calc.)

In this work we were unable to calculate the orbital Lande factors α and α' as also the reduced spin-orbit constant $\lambda_{\parallel}$ and $\lambda_{\perp}$, by fitting the experimental results to the theoretical expressions, as was done by earlier workers mentioned above, because these factors appear in the theoretical equations as P_i's and Q_i's (where $i = \parallel$ and $\perp$, $P_{\parallel} = \alpha\lambda_{\parallel}$, $P_{\perp} = \alpha'\lambda_{\perp}$, $Q_{\parallel} = \alpha K_{\parallel}$, $Q_{\perp} = \alpha' K_{\perp}/2$). Consequently we cannot determine the six unknown quantities α, α', λ_i and κ_i from the four known values P_i's and Q_i's given in table 4a. However, we can estimate the possible range of values for the α's as well as the λ's by assigning numerical values of κ's within a small range of probable values as shown in table 5. Inspection of table 5 shows that it is very likely that the covalency reduction factors κ's are close to the values 1 to 0·9, as otherwise the Lande factors deviate too much from the value of $\alpha = 3/2$ for a O_h symmetry and the spin-orbit coupling

constants are also reduced abnormally. Usually, this reduction should not be more than 10 to 20% for the semi-ionic salts considered here as shown by other similar octahedral complexes of the iron-group of elements (Owen 1955).

From table 4a, we find that as the temperature deviates from 100°K there are small and systematic deviations between the theoretical and experimental results for ΔK and $\bar{K}$, if we make the fittings of magnetic data to remain consistent with the observed optical separations, about the assignments of which there is no reasonable doubt. These deviations are real and may be due to the fact that with the anisotropic thermal expansion of the lattice the parameters P's and Q's may appreciably change, since the covalency overlaps are structure sensitive properties. Further, the anisotropic ligand field may also change, altering the value of Δ, as suggested by Bose *et al* (1951), in explaning the anomalies in the magnetic behaviour of a large number of crystals and by Holmes *et al* (1964) in explaining the blue-shifts for $CoSO_4$, $7H_2O$ spectra It is not mathematically possible to calculate the variation in the P's, Q's and Δ with temperature, since the number of parameters would be larger than the number of independent equation

TABLE 5. $Co(NH_4SO_4)_2\ 6H_2O$ (Free ion value for λ in Co^{2+} ion is 180 cm^{-1})

k	$\lambda_{\|}(cm^{-1})$	$\lambda_{\perp}(cm^{-1})$	α	α'
1	170	150	1 14	1.55
0 9	153	134	1 26	1 72
0.8	137	120	1.42	1 94
0.7	120	104	1.63	2.22

In the case of $Co(KSO_4)_2.6H_2O$, e.p.r study Bleaney *et al* (1951) have shown a small orthorhombicity in the g-values, so that the expressions for uniaxial symmetry, as assumed by the earlier workers and by us, is not exactly applicable here Such differences in symmetry in the ammonium and potassium salt may explain the rather large difference in the Δ values, namely 700 cm^{-1} and 300 cm^{-1} respectively, (calculated on the basis of approximate uniaxial symmetry) and also the large deviations between the experimental and theoretical results for this salt The corresponding absorption bands could not be resolved sufficiently to indicate the differences in the symmetry of the two salts. Resolutions of the spectra at hydrogen temperatures for these rsalts may be expected to give the splittings of the ground $^4T_{1g}$ level due to the lower symmetric fields and may also help to obtain the other parameters in these salt more accurately.

ACKNOWLEDGEMENT

The authors are grateful to Prof. A. Bose, D.Sc , F.N.A. for suggesting the problem and for his constant guidance and criticism.

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